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(54) **Method of making fused silica**

Verfahren zur Herstellung von Quarzglas

Procédé de fabrication de verre de silice

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(73) Proprietor: **Corning Incorporated**  
Corning New York 14831 (US)

(72) Inventors:  
• Blackwell, Jeffery Lynn,  
Corning Incorporated  
Corning, New York 14831 (US)  
• Dobbins, Michael Sean,  
Corning Incorporated  
Corning, New York 14831 (US)  
• McLay, Robert Ernest,  
Corning Incorporated  
Corning, New York 14831 (US)

• Truesdale, Carlton Maurice,  
Corning Incorporated  
Corning, New York 14831 (US)

(74) Representative: **Marchant, James Ian et al**  
Elkington and Fife,  
Prospect House,  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)

(56) References cited:  
EP-A- 0 038 900 EP-A- 0 092 024  
EP-A- 0 471 139 WO-A-90/10596  
FR-A- 2 451 343 US-A- 4 501 602

• PATENT ABSTRACTS OF JAPAN vol. 13, no. 556  
(C-664) 11 December 1989 & JP-A-01 230 444  
• PATENT ABSTRACTS OF JAPAN vol. 9, no. 254  
(C-308) 11 October 1985 & JP-A-60 108 338  
• PATENT ABSTRACTS OF JAPAN vol. 9, no. 233  
(C-304) 19 September 1985 & JP-A-60 090 838

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## Description

The present invention relates to a method of making high purity fused silica.

Various processes are known in the art that involve the production of metal oxides from vaporous reactants. The most basic requirements of such processes necessitate a feedstock solution, a means of generating and transporting vapors of the feedstock solution (hereafter called vaporous reactants) and an oxidant to a reaction site, and a means of catalyzing oxidation and combustion coincidentally, producing finely divided, spherical aggregates, called soot. This soot may be collected in any number of ways, ranging from a collection chamber to a rotating mandrel, and simultaneously or subsequently heat treated to form a non-porous, transparent, high purity glass article. The means for executing these reactions is usually a specialized piece of equipment with a unique arrangement of nozzles and burners.

Much of the initial research focused on the production of fused silica. Selection of the appropriate feedstock was found to be as important in the production of high purity fused silica as the equipment used in its production. Consequently, a material was identified that could generate the needed vapor pressure of 200 - 300 mm at temperatures below 100°C; the high vapor pressure of silicon tetrachloride (SiCl<sub>4</sub>) isolated it as a convenient vapor source for soot generation, thus launching the discovery and use of a series of similar chloride-based feedstocks. This factor, more than any other, is responsible for the presently accepted use of SiCl<sub>4</sub>, GeCl<sub>4</sub>, POCl<sub>3</sub>, and BCl<sub>3</sub> as vapor sources, even though these materials have certain chemically undesirable properties.

SiCl<sub>4</sub> has been the industry standard among metal-source vaporous reactants used over the years for the production of high purity silica glasses. As disclosed in U.S. Patent 3,698,936, one of several reactions may be employed to produce high purity fused silica via oxidation of SiCl<sub>4</sub>; namely:



whereby burners or jet assemblies are utilized in feeding the reactant gases and vapors to a reaction space. There are inherent economic disadvantages to each of these reactions.

These reactions, which oxidize SiCl<sub>4</sub> through pyrolysis and hydrolysis, have the disadvantage of producing a very strong acid by-product. While the first two reactions occur theoretically, it is likely that an auxiliary fuel is needed to achieve pyrolytic temperature, thus leading to hydrolysis of the silicon tetrachloride and formation of hydrochloric acid (HCl). Such a by-product is not only a detriment to many deposition substrates and the reaction equipment, but also has to be treated before being released into the environment. Such abatement systems have proven to be very expensive due to down-time, loss, and maintenance of equipment caused by the corrosiveness of HCl.

As an alternative, high purity fused quartz or silica may also be produced by thermal decomposition and oxidation of silane, a compound that requires taking safety measures in handling due to the violent reaction caused when air is introduced into a closed container of silane. Silane is commonly reacted with carbon dioxide, nitrous oxide, oxygen, or water to produce a high purity material that is useful in producing, among other things, semiconductor devices, while emitting a host of by-products such as carbon monoxide, hydrogen, and nitrogen. However, silane has proven to be much too expensive and reactive to be considered for commercial use except possibly for extremely high purity applications.

The novelty of the invention described herein lies in the replacement of SiCl<sub>4</sub> in vapor deposition processes with a chloride-free, silica-source compound, thus greatly reducing, if not eliminating, the production of HCl. The advantages of operating under a chloride-free system include: reduced pollution abatement requirements and reduced equipment losses and maintenance due to the corrosive nature of HCl.

The teachings of the instant invention are easily adapted to known methods of producing high purity fused silica by flame pyrolysis or hydrolysis, such as those disclosed in the early patents by Nordberg (U.S. Patent 2,239,551) in 1941 and Hyde (U.S. Patent 2,272,342) in 1942. It is anticipated that this process alteration may be adapted to a variety of deposition/collection techniques as well. Therefore, it is an object of this invention to provide an improved method of making high purity fused silica by utilizing alternative silicon-source compounds, thus greatly reducing, if not eliminating, the need for elaborate pollution abatement equipment.

While it is recognized that the primary application of the instant invention relates to the production of fused silica, the technology applied herein is generally applicable in instances where a high purity metal oxide glass is desired.

It is a further object of this invention to provide an improved method of making high purity metal oxide glasses through the use of alternative metal oxide source compounds, thereby greatly reducing the need for expensive pollution abatement systems.

The process according to the present invention utilizes halide-free, silicon-containing compounds as a replacement for the halide-based source feedstocks that are often oxidized by flame hydrolysis or pyrolysis, to produce transparent,

high-purity silica glass articles. The production of fused silica glass through the use of pyrolyzable and/or hydrolyzable halide-free, silicon-containing compounds as the feedstock components results in carbon dioxide and water as the by-products.

EP-A-0 471 139, related to the inventors of the present application, published on 19.02.92 but with an earlier priority date, describes polymethylsiloxanes as halide-free, silicon-containing compounds for use as replacements for halide-based source feedstocks, with polymethylcyclotrisiloxanes being the preferred members of that group of compounds. Thus, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and hexamethylcyclotrisiloxane were disclosed as being especially suitable as halide-free feedstocks.

Parallel application EP-A-0 529 190, corresponding to US-A-5 154 744, is directed to the production of high purity fused silica glass doped with titanium wherein fused silica glass is doped through the use of a halide-free, titanium-containing compound in vapor form capable of being converted through thermal decomposition with oxidation or flame hydrolysis to  $\text{TiO}_2$  selected from the group consisting of titanium, isopropoxide, titanium ethoxide, titanium-2-ethylhexyloxy, titanium cyclopentyloxy, a titanium amide, and mixtures thereof.

WO-A-90 10596 describes a process for the manufacture of a synthetic silica product by vapor-phase oxidation of a silica precursor material in a flame, not less than 60% of the silica in the deposited product being derived by oxidation of: (A) one or more straight chain volatile silicon compounds of the general formula:  $\text{R}_3\text{Si}(\text{SiR}_2\text{O})_n\text{SiR}_3$  and/or (B) one or more cyclic volatile silicon compounds of the general formula:  $\text{Si}_n\text{O}_n(\text{R})_{2n}$ . Doped or undoped fume powder, porous silica soot or fully densified bodies may be produced by the process.

Further laboratory work has demonstrated that operable halide-free, silicon-containing feedstocks need not be limited to the polymethylsiloxanes. That is, we have found that organosilicon materials satisfying the following three criteria can be suitably utilized as substitutes for halide-containing compounds:

- (1) an operable organosilicon-R compound (R is an element of the Periodic Table) will have a Si-R bond dissociation energy that is no higher than that of the Si-O bond;
- (2) an operable organosilicon-R compound will exhibit a boiling point no higher than  $350^\circ\text{C}$  and preferably a significant vapor pressure at temperatures below  $250^\circ\text{C}$ ; and, in the interest of safety,
- (3) an operable organosilicon-R compound will, upon pyrolysis and/or hydrolysis, produce minimal decomposition products besides  $\text{SiO}_2$ , i.e. at a level which is to be environmentally safe or the emissions are below acceptable governmental standards.

That fundamental discovery resulted from our finding of a large number of halide-free, silicon-source compounds exhibiting a variety of bonding arrangements to the silicon atom that have proven to be useful as substitutes for halide-base materials. Two groups of compounds which have been found to be especially useful are categorized below according to the bonding arrangement in the basic structure:

- (1) organosilicon-nitrogen compounds, having a basic Si-N-Si structure, such as aminosilanes, linear silazanes, and cyclosilazanes, wherein a nitrogen atom and a single element or group of elements are bonded to the silicon atom; and
- (2) siloxasilazanes, having a basic Si-N-Si-O-Si structure, wherein a nitrogen atom and an oxygen atom are bonded to the silicon atom.

These compounds have a significant vapor pressure when heated above  $150^\circ\text{C}$ . The prior art discloses halide-containing silanes as sources for producing silica (e.g.,  $\text{Si-R}_m\text{Cl}_{2-m}$ , where R is an organic group). Our experiments indicate that the presence of a halide is not necessary; indeed, organosilicon-R compounds free from halides produce silica having very high purity.

Tris (trimethylsilyl) ketenimine, nonamethyltrisilazane, and octamethylcyclotetrasilazane are illustrative of an operable aminosilane, a linear silazane, and a cyclosilazane, respectively, and hexamethylcyclotrisiloxazane is illustrative of an operable siloxasilazane. The representative compounds in each of these classes of compounds comprise the preferred embodiment of each respective class.

It will be appreciated that, similarly to the current commercial processes for doping fused  $\text{SiO}_2$  articles produced via the thermal decomposition with oxidation or hydrolysis of  $\text{SiCl}_4$  with various metals in order to modify the chemical and/or physical properties thereof, the fused  $\text{SiO}_2$  articles prepared in accordance with the present invention can likewise be doped with metals. For example, fused silica articles have been doped commercially with  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{TiO}_2$  utilizing halide-containing compounds of aluminum, boron, germanium, phosphorous, and titanium, respectively. Like dopants can be utilized in the present inventive process but would, of course, provide a source of halide emissions. Consequently, to eliminate point source emissions of halides, organo-metallic compounds of the dopant metals will be employed. For example, isopropyl titanate and titanium ethoxide can be used as sources of titanium and methyl borate can furnish the dopant source of boron.

Further examples of operable organometallic dopants are found in U.S. Patent No. 4,501,602 (Miller et al.). That

patent describes the production of glass/ceramic articles via a vapor phase oxidation process wherein  $\beta$ -diketonate complexes selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, and IVB, and the rare earth series of the Periodic Table are vaporized, the vapor is transported to an oxidation site, such as a burner or a hot plasma zone which is adjacent to a deposition substrate or within a deposition tube, and oxidized in the vapor phase to form particulate metal oxide soot.  $\beta$ -diketonate complexes are also available of metals in Group VA of the Periodic Table, notably vanadium and tantalum. Accordingly, the use of  $\beta$ -diketonate complexes provides a vaporizable source for a wide variety of dopant metals. In summary, our invention comprehends doping of fused  $\text{SiO}_2$  articles with  $\text{P}_2\text{O}_5$  and/or at least one metal oxide selected from Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table.

#### Brief Description of Drawings

FIGURE 1 comprises a schematic representation of the apparatus and process for forming large masses of fused silica.

FIGURES 2 and 2A comprise schematic representations of the apparatus and process for depositing silica soot on a rotating mandrel to form a porous blank or preform.

FIGURE 3 comprises a schematic representation of a heating chamber wherein the porous blank is fired in an atmosphere of helium and chlorine to full consolidation to a non-porous body.

This invention is illustrated by the following examples:

#### Comparative Example 1

Figure 1 illustrates a system wherein  $\text{SiCl}_4$  was replaced with an octamethylcyclotetrasiloxane OMCTS feedstock 1 in a commercial furnace to produce boules of high purity fused silica. An inert gas, nitrogen, was used as the carrier gas and a bypass stream of nitrogen 2 was introduced to prevent saturation of the vaporous stream. The vaporous reactant was passed through a distribution mechanism 3 before being transported to the reaction site wherein a number of burners 4 are contained in close proximity to a furnace crown 5. These burners combusted and oxidized the vaporous reactants at a temperature greater than  $1700^\circ\text{C}$ , directing high purity metal oxide soot and heat downward through the refractory furnace crown 5 where it is immediately deposited and consolidated to a nonporous mass on a hot bait 6.

In the production of relatively large boules, the maximum soot collection efficiencies measured using  $\text{SiCl}_4$  as the feedstock have ranged about 60-70%. Extensive trials have indicated that the average deposition efficiency for boule process utilizing OMCTS as the source material is at least 10% higher than those processes using  $\text{SiCl}_4$ . Therefore, in addition to eliminating halide emissions, the quantity of particulate emissions is likewise reduced.

It is well recognized in the art that processing of the feedstock requires apparatus and transfer system capable of vaporizing the feedstock and delivering it in the vapor state. Somewhat higher temperatures are necessary due to its lower vapor pressure when compared to  $\text{SiCl}_4$ .

#### Example 2

To broaden the general class of alternative non-polluting sources of silica, a number of organometallic compounds were investigated with several objectives in mind. First, we wanted to demonstrate that silica soot can, indeed, be made from the organosilicon compounds of the instant invention. Second, we wanted to determine whether the linear siloxanes would produce silica soot as has been demonstrated with the cyclosiloxanes (e.g. OMCTS). Third, we wanted to determine whether the Si-N bond of organosilicon-nitrogen compounds could be broken and replaced by a Si-O bond of higher bond strength during the combustion process. Finally, when decomposed to make high purity fused silica, the by-products of said organo-silicon compounds and the consequential emissions of said organosilicon compounds must be classified as environmentally safe by the OSHA (Occupational Health and Safety Administration) and the EPA (Environmental Protection Agency).

Experimental samples were either directly metered as liquid to a flash vaporizer, or as in one case, melted and bubbled over to the fume tube of a standard methane/oxygen ring burner. Octamethylcyclotetrasilazane, tris (trimethylsilyl) ketenimine, and octamethyltrisiloxane were obtained through commercial manufacturers and soot was produced from each. The soot was collected and chemically analyzed to determine the silicon, nitrogen, and oxygen content of each. The error of the wt.%  $\text{O}_2$  is shown parenthetically to the last place indicated.

TABLE I

Compound	%Nitrogen	%Oxygen	%Silicon
octamethyltrisiloxane	< 0.01	53.7(4)	46.6
tris (trimethylsilyl) ketenimine	< 0.01	53.4(4)	46.6
octamethylcyclotetrasilazane	< 0.01	53.1(4)	46.6

As can be seen from Table I, the linear siloxane octamethyltrisiloxane, an organosilicon-oxygen compound, the organosilicon-nitrogen compounds tris (trimethyl) ketenimine and octamethylcyclotetrasilazane pyrolyzed/hydrolyzed to yield an amount of  $\text{SiO}_2$  comparable to that produced with octamethylcyclotetrasiloxane, the most preferred polymethylcyclosiloxane described in EP-A-0 471 139.

The bond energy of the Si-O bond is  $191.1 \pm 3.2$  kcal/mole and that of the Si-N bond is  $105 \pm 9$  kcal/mole. Thus, the energy of the Si-N bond is about  $86 \pm 10$  kcal/mole less than that of the Si-O bond. The utility of tris (trimethyl) ketenimine in yielding  $\text{SiO}_2$  confirms one of the above criteria which an operable organosilicon-R compound must obey; viz., that the dissociation energy of the Si-R bond must not exceed that of the Si-O bond. That factor, i.e., the presence of a Si-N bond, explains the effectiveness of siloxasilazanes in producing high purity  $\text{SiO}_2$  when subjected to a pyrolysis/hydrolysis reaction with oxygen. The reaction products will essentially track those resulting from the pyrolysis/hydrolysis of an organosilicon-nitrogen compound.

A practical advantage which these materials have when compared to octamethylcyclotetrasiloxane is that the purity thereof is much higher. The specifically-described organosilicon compounds of the instant invention are generally free from the high levels of alkali metal and transition metal impurities found in OMCTS. OMCTS is reported to be 95% pure, while the cited organosilicon compounds of the instant invention have a reported 99% purity. The 5% level of impurities for OMCTS consists of higher molecular weight cyclosiloxanes not being totally separated by fractional distillation, and trace amounts of alkali and transition metals.

In waveguide processing, however, the requisite step of chlorine drying not only removes water, but also removes the alkali and transition metal impurities to a level < 10 ppb, the level required when producing low attenuation fiber. Thus, the effect of these alkali and transition metal impurities is neutralized in the traditional processing sequence of optical waveguide fiber.

Most of the processes being developed by industry today for the manufacture of optical waveguides employ the chemical vapor deposition (CVD) concept or a modified version thereof. In a CVD experiment, each of the component liquids is heated to a constant temperature at which enough vapor pressure is generated to produce a reasonable rate of deposition. The individual vapors are entrained in a carrier gas stream, mixed together prior to combustion to ensure homogeneous output, and then passed through a burner flame, usually a natural gas/oxygen mixture, containing excess oxygen. The vapors in the mixture are converted to their respective oxides and exit the burner orifice to form a stream of the volatile gases and finely-divided, spherical particles of soot. The soot is collected on a mandrel (OVD) or bait tube [Axial Vapor Deposition (AVD)] and deposited in thin layers. The final product of soot collection, the porous preform, is then subjected to high temperature in which the preform consolidates to a nonporous monolithic glassy body.

In usual practice, the optical waveguide process is a three-step process. In the first stage of optical fiber fabrication, oxygen, the carrier gas, is bubbled through a liquid feedstock of  $\text{SiCl}_4$  that is maintained at a constant temperature. The resulting vaporous reactant is transported to a reaction site, such as a burner, via a carrier gas, wherein the vaporous gas streams are combusted in a burner flame fueled with natural gas and oxygen. The presence of oxygen serves to convert the vaporous reactants to their respective oxides, exiting the burner orifice to form a stream of volatile gases and finely-divided, spherical particles of soot that are deposited onto a substrate, forming a porous blank or preform of opaque, white silica soot. Water, HCl, and carbon dioxide are emitted as byproducts of this reaction.

In the second stage the blank or preform is subsequently heat treated in a helium/chlorine atmosphere to full consolidation. In the third and final stage, conventional fiber-draw technology is utilized in extracting optical waveguide fiber from the preform.

That process is illustrated in Figure 2 and is equally applicable with the materials of the present invention. Hence, as is indicated in Figure 2,  $\text{SiCl}_4$  is replaced with one of the organosilicon-R compounds as feedstock 7 in the OVD process using standard OVD equipment and conventional OVD processing techniques used in making optical waveguides. An inert gas, nitrogen, is employed as the carrier gas and a methane/oxygen mixture is employed as the burner flame fuel, whereby combustion and oxidation are induced at the reaction site 8. The resulting soot is deposited on a rotating rod 9, thus forming a preform or blank 10 of silica soot. The preform is then heat treated in a consolidation furnace 11, in a  $\text{He/Cl}_2$  atmosphere to full consolidation. Conventional fiber draw techniques are then employed in making optical

waveguide fiber. No additional equipment is required, but the delivery system has to be capable of vaporizing the material and delivering it to a standard OVD burner in the vapor state.

# Claims

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1. A method for making high purity fused silica by an outside vapor deposition process comprising the steps of:

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(a) producing a gas stream containing an organosilicon-compound in vapor form capable of being converted through thermal decomposition with oxidation or flame hydrolysis to  $\text{SiO}_2$ ;  
 (b) passing said gas stream into the flame of a combustion burner to form amorphous particles of fused  $\text{SiO}_2$ ;  
 (c) depositing said amorphous particles onto a support; and  
 (d) consolidating the deposit of amorphous particles into a non-porous transparent glass body;  
 wherein said organosilicon compound is a halide-free, organosilicon-R compound in vapor form having an Si-N-Si or a Si-N-Si-O-Si structure and having the following properties:

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- (1) a Si-R bond dissociation energy that is no higher than the dissociation energy of the Si-O bond;
- (2) a boiling point no higher than  $350^\circ\text{C}$ ; and
- (3) which, upon pyrolysis and/or hydrolysis, will produce minimal decomposition products beside  $\text{SiO}_2$ .

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2. A method according to claim 1 wherein the deposit of amorphous silica particles is consolidated either simultaneously with the deposition or subsequently thereto.

3. A method according to claim 1 or 2, which further comprises

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(a) producing a gas stream containing the halide-free, silicon-containing compound in vapor form and a compound in vapor form capable of being converted through thermal decomposition with oxidation or flame hydrolysis to  $\text{P}_2\text{O}_5$  and/or at least one metal oxide selected from the Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table; and

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(b) passing said gas stream into the flame of a combustion burner to form amorphous particles of fused  $\text{SiO}_2$  doped with  $\text{P}_2\text{O}_5$  and/or at least one metal oxide selected from the Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table.

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4. A method according to claim 3 wherein said compound capable of being converted to  $\text{P}_2\text{O}_5$  and/or at least one metal oxide selected from the Groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, and the rare earth series of the Periodic Table is a halide-free compound.

5. A method according to any of claims 1 to 4 wherein in a further step e) optical waveguide fibers are drawn from the glass body.

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6. A method according to any of claims 1 to 5 wherein the organosilicon-R compound is an organosilicon-nitrogen compound, a siloxasilazane or a mixture thereof.

7. A method according to any of claims 1 to 6 wherein the organosilicon-R compound is an aminosilane, a linear silazane, or a cyclosilazane.

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8. A method according to claim 7 wherein the organosilicon-R compound is tris (trimethylsilyl) ketenimine, nonamethyltrisilazane, octamethylcyclotetrasilazane, or hexamethylcyclotrisiloxazane.

# Patentansprüche

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1. Verfahren zur Herstellung von Quarzglas mit hoher Reinheit durch ein Verfahren zur Niederschlagung bzw. Abscheidung aus der Dampfphase auf der Außenseite mit den nachfolgenden Schritten:

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(a) Bereitstellen eines Gasstroms mit einer Organo-Siliciumverbindung in Dampfform, die durch thermischen Abbau durch Oxidation oder Flamhydrolyse zu  $\text{SiO}_2$  umwandelbar ist;  
 (b) Leiten des Gasstromes in die Flamme eines Brenners zur Bildung amorpher Teilchen aus geschmolzenem  $\text{SiO}_2$ ;  
 (c) Abscheidung der amorphen Teilchen auf einem Träger; und  
 (d) Konsolidieren der Abscheidung amorpher Teilchen zu einem nichtporösen transparenten Glaskörper,

wobei die Organo-Siliciumverbindung eine halogenfreie Organo-Silicium-R-Verbindung in Dampfform mit einer Si-N-Si oder einer Si-N-Si-O-Si-Struktur ist und die nachfolgenden Eigenschaften aufweist:

- (1) eine Si-R-Bindungs-Spaltungsenergie, die nicht höher ist als die Spaltungsenergie der Si-O-Bindung;
  - (2) einen Siedepunkt von nicht über 350°C; und
  - (3) die, bei Pyrolyse und/oder Hydrolyse, neben SiO<sub>2</sub> nur minimale Abbauprodukte ergibt.
2. Verfahren nach Anspruch 1, wobei die Abscheidung amorpher Siliciumdioxidteilchen entweder gleichzeitig mit der Abscheidung oder anschließend konsolidiert wird.
3. Verfahren nach Anspruch 1 oder 2, weiterhin umfassend
  - (a) Bereitstellen eines Gasstroms, der die halogenfreie, Silicium enthaltende Verbindung in Dampfform und eine Verbindung in Dampfform enthält, die durch thermischen Abbau durch Oxidation oder Flammhydrolyse zu P<sub>2</sub>O<sub>5</sub> und/oder wenigstens einem Metalloxid, ausgewählt aus den Gruppen IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA und den Seltenerdreihen des Periodensystems, umwandelbar ist, und
  - (b) Einleiten des Gasstromes in die Flamme eines Brenners zur Bildung amorpher Teilchen aus geschmolzenem SiO<sub>2</sub>, dotiert mit P<sub>2</sub>O<sub>5</sub> und/oder wenigstens einem Metalloxid, ausgewählt aus den Gruppen IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA und den Seltenerdreihen des Periodensystems.
4. Verfahren nach Anspruch 3, wobei die Verbindung, die zu P<sub>2</sub>O<sub>5</sub> und/oder wenigstens einem Metalloxid, ausgewählt aus den Gruppen IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA und den Seltenerdreihen des Periodensystems umwandelbar ist, eine halogenfreie Verbindung ist.
5. Verfahren nach einem der Ansprüche 1 - 4, wobei in einem weiteren Schritt e) optische Wellenleiterfasern aus dem Glaskörper gezogen werden.
6. Verfahren nach einem der Ansprüche 1 - 5, wobei die Organo-Silicium-R-Verbindung eine Organo-Silicium-Stickstoff-Verbindung, ein Siloxasilazan oder eine Mischung hieraus ist.
7. Verfahren nach einem der Ansprüche 1 - 6, wobei die Organo-Silicium-R-Verbindung ein Aminosilan, ein lineares Silazan oder ein Cyclosilazan ist.
8. Verfahren nach Anspruch 7, wobei die Organo-Silicium-R-Verbindung Tris(trimethylsilyl)-ketenimin, Nonamethyltrisilazan, Octamethylcyclotetrasilazan oder Hexamethylcyclotrisiloxazan ist.

## Revendications

1. Un procédé pour préparer de la silice fondue de haute pureté par un processus de dépôt de vapeur par l'extérieur, comprenant les opérations consistant :
  - (a) à produire un courant gazeux contenant un composé organosilicié sous forme de vapeur se prêtant à être transformé en SiO<sub>2</sub> par décomposition thermique avec oxydation ou hydrolyse à la flamme ;
  - (b) à faire passer ledit courant gazeux dans la flamme d'un brûleur à combustion pour former des particules amorphes de silice fondue ;
  - (c) à déposer lesdites particules amorphes sur un support ; et
  - (d) à consolider le dépôt de particules amorphes en un corps en verre transparent non poreux, ledit composé organosilicié étant un composé organosilicié-R, exempt d'halogénure, sous forme de vapeur ayant une structure Si-N-Si ou Si-N-Si-O-Si et ayant les propriétés suivantes :
    - (1) une énergie de dissociation de la liaison Si-R qui n'est pas supérieure à l'énergie de dissociation de la liaison Si-O ;
    - (2) un point d'ébullition non supérieur à 350 °C ; et
    - (3) qui, par pyrolyse et/ou hydrolyse, produira le moins possible de produits de décomposition à côté de SiO<sub>2</sub>.
2. Un procédé selon la revendication 1 dans lequel le dépôt de particules de silice amorphe est consolidé soit simultanément, soit postérieurement au dépôt.

## 3. Procédé selon la revendication 1 ou 2 comprenant en outre

(a) la production d'un courant gazeux contenant sous forme de vapeur le composé silicié exempt d'halogénure et un composé sous forme de vapeur se prêtant à être transformé par décomposition thermique avec oxydation ou hydrolyse à la flamme en  $P_2O_5$  et/ou en au moins un oxyde de métal choisi parmi les Groupes IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB et VA et la série des terres rares du Tableau périodique ; et

(b) à faire passer ledit courant gazeux dans la flamme d'un brûleur à combustion pour former des particules amorphes de silice fondue dopée par du  $P_2O_5$  et/ou par au moins un oxyde de métal choisi parmi les Groupes IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA et la série des terres rares du Tableau périodique.

4. Un procédé selon la revendication 3 dans lequel ledit composé se prêtant à être transformé en  $P_2O_5$  et/ou en au moins un oxyde de métal choisi parmi les Groupes IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB et VA et la série des terres rares du Tableau périodique est un composé exempt d'halogénure.

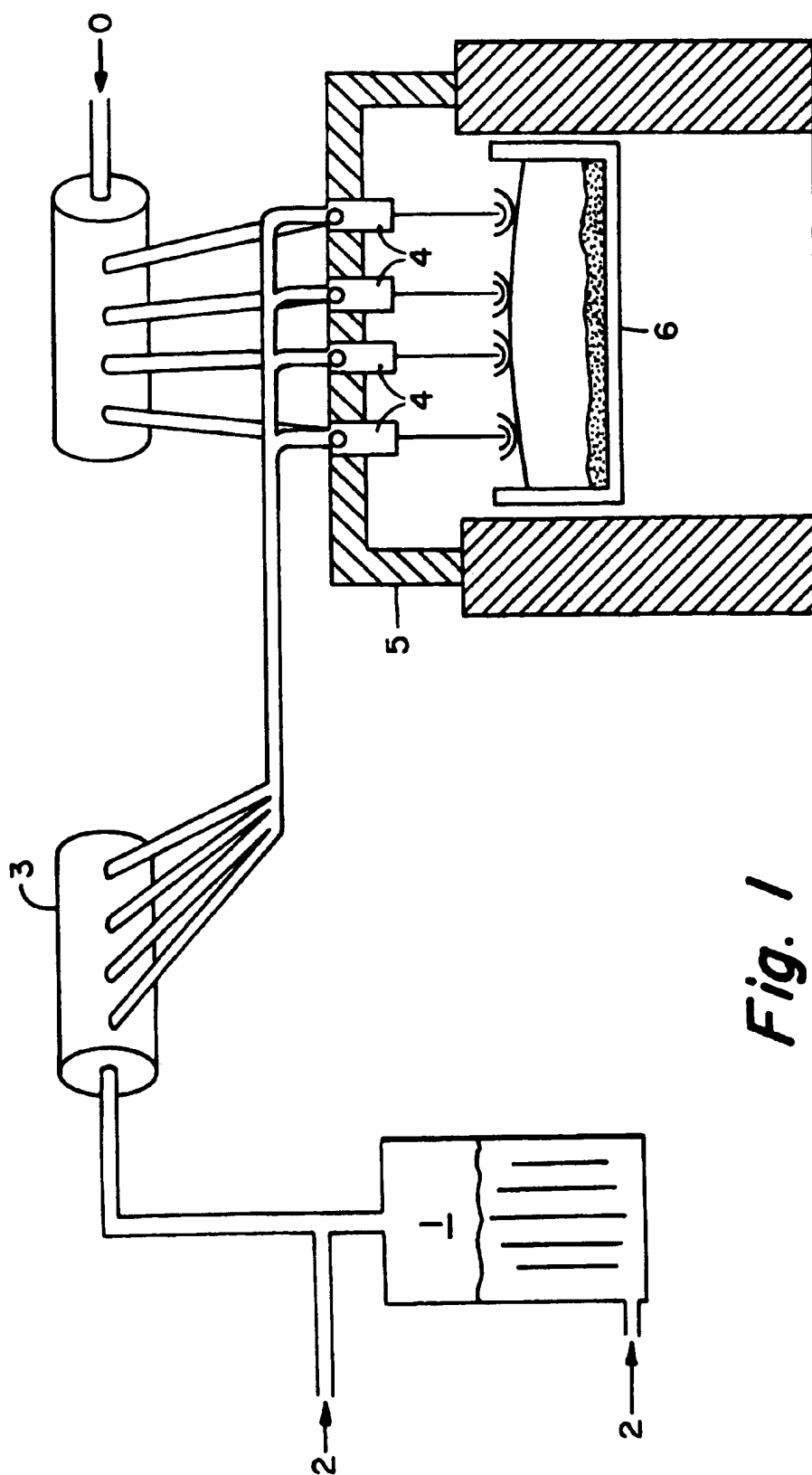
5. Un procédé selon l'une quelconque des revendications 1 à 4 comprenant une opération supplémentaire dans laquelle des fibres de guide d'ondes optique sont étirées à partir du corps en verre.

6. Un procédé selon l'une quelconque des revendications 1 à 5 dans lequel le composé organosilicié-R est un composé organosilicié-azote, un siloxasilazane ou un mélange de tels composés.

7. Un procédé selon l'une quelconque des revendications 1 à 6 dans lequel le composé organosilicié-R est un aminosilane, une silazane linéaire ou un cyclosilazane.

8. Un procédé selon la revendication 7 dans lequel le composé organosilicié-R est la tris(triméthylsilyl)céténimine, le nonaméthyltrisilazane, l'octaméthylcyclotétrasilazane ou l'hexaméthylcyclotrisiloxazane.





*Fig. 1*

